

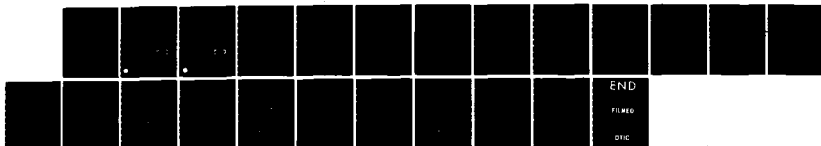
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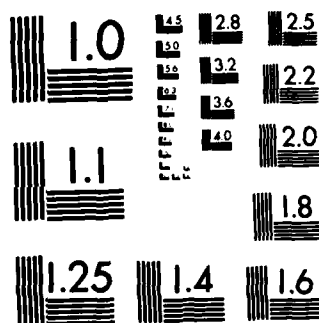
MONITORING CURE OF EPOXY RESINS USING A
MICRODIELECTROMETER(U) WESTINGHOUSE RESEARCH AND
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MONITORING CURE OF EPOXY RESINS
USING A MICRODIELECTROMETER

Z. N. Sanjana and R. L. Selby

Technical Report No. 1

September 1984

Department of the Navy
Office of Naval Research
Contract No. N00014-82-C-0164

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Block No. 20 (Abstract)

Microdielectrometry is a recent advancement in monitoring the cure of resins using dielectric techniques. It utilizes a solid state chip roughly $.075'' \times .075''$ as the probe, and has on-chip amplification of the signal which permits interrogation of the material at frequencies as low as 1 Hz. This paper discusses cure monitoring of resins utilizing microdielectrometry and compares the technique and instrumentation to conventional dielectrometry. Data on an anhydride cured system and an aromatic amine cured system cured under isothermal and temperature variant conditions are presented. Results show that microdielectrometry can be used to follow cure of epoxy resins. Absolute measurements of permittivity and loss factor can be made and they provide information on the mechanisms that produce the observed changes. The present packaging of the chip is unsuitable for use with composites.

FORWARD

The following report describes part of the work performed under ONR Contract No. N00014-82-C-0164, "Monitor Cure of Composites and Evaluate Cure Monitoring Procedures". This report (Report No. 1) covers the work done with Micromet System I which used a T0-8 header mounted dielectric sensor. Report No. 2 will cover the work done using a flexible flat cable mounted sensor using System I instrumentation. The final Report No. 3 will cover work done with Micromet System II in which the gain phase meter of System I is replaced with a Micromet developed fourier transform analyzer which increases system sensitivity and reduces system noise.

This program was administered for ONR by Dr. L. H. Peebles, Jr. The program was conducted entirely at the Westinghouse Electric Corp., R&D Center, in the Polymer & Composite Research Department. Z. N. Sanjana was the Principal Investigator.

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1. INTRODUCTION

As thermosetting resins and advanced composites made from them begin to be used in critical applications it becomes necessary to monitor the cure of the thermosetting resins within the confines of the processing equipment. Such measurements of cure have been carried out by several investigators using a dielectric technique generally called dielectric analysis.⁽¹⁻⁶⁾ In conventional dielectric analysis the sample to be examined is placed between two parallel conducting plates or electrodes and the ac capacitance and dissipation factor are measured using a device called an automatic dielectrometer. One such automatic dielectrometer, popularly called by its acronym Audrey has been frequently used. It provides a continuous output of dissipation factor and capacitance as a function of time, temperature and frequency (from 0.1 kHz to 100 kHz). It has been successfully used in studying parameters affecting cure⁽¹⁻³⁾, in situ monitoring of cure in an autoclave⁽⁴⁾, and features of the dielectric output have been related to changes in chemistry⁽⁵⁾.

There are certain problems associated with conventional dielectrometry, mainly centered around the use of the parallel plate geometry for electrodes. For in situ measurement of cure the placement and intrusiveness of the electrodes becomes an issue. Also, since parallel plate spacing can change during cure, it is difficult to deduce from the capacitance and dissipation factor curves the fundamental dielectric properties, permittivity and loss factor. The use of conductive fibers such as graphite and boron require special treatment of the sample geometry. Furthermore, conventional dielectric methods depend on measuring the capacitive current flowing through the sample space which at low frequencies become very small and therefore signal-to-noise ratios become small.

Microdielectrometry^(6,7) is a technique developed as one approach to overcome some of the problems described above. Integrated circuit

technology is used to develop a miniaturized probe that combines a small size with built-in amplification to measure dielectric properties of polymers at frequencies as low as 1 Hz. The integrated circuit device consists of a planar interdigitated electrode structure with a pair of matched field effect transistors. The electrode geometry does not change during cure and is reproducible from device to device.

2. EXPERIMENTAL

2.1 Microdielectrometry

System I consisting of instrumentation, software and the integrated circuit cure sensor was obtained from Micromet Instruments, Inc.⁽⁸⁾ It is shown schematically in Figure 1. The technology and relative advantages of microdielectrometry have been fully described by Senturia and co-workers.^(6,7,9) The system, in essence, takes the relative gain and phase of the sensor output compared to sensor input (imposed sinusoidal voltage under command from a programmed computer) and using an internally stored calibration converts the data into permittivity (ϵ'), loss factor (ϵ''), and their ratio the loss tangent or dissipation factor ($\tan \delta = \epsilon''/\epsilon'$). Thus ϵ' and ϵ'' can be measured for any material that is on the surface of the integrated circuit chip or sensor. The sensor consists of a 0.075" x 0.075" integrated circuit mounted at present on a TO-8 transistor header. Both electrodes used in the dielectric measurement are placed on the same surface to form an interdigitated capacitor and on-chip amplification produces high signal-to-noise ratios.⁽⁷⁾

The present package is not suitable for use with composites because the fine wires that connect the sensor chip to the pads of the TO-8 header protrude above the surface of the header and are extremely fragile. Thus, embedding the sensor into a composite, at present, is not feasible. However, a "flat" ribbon cable package is being developed by Micromet and when it becomes available, evaluation of the cure of composites will become feasible.

Calibration of the system is not easy because well-known liquid standards with appropriate loss and permittivity characteristics are not available. However, calibration of the sensors using air as a known dielectric revealed a systematic error in the conversion of gain-phase data to permittivity-loss factor. The error occurs at frequencies above 1 kHz and increases with frequency. This was discussed with the supplier and since this is a problem with the internally stored calibration involving the geometry of the chip sensor, a recalibration for the next design sensors would try to eliminate this problem. At present we are restricted to using frequencies below 1 kHz.

In a further attempt to calibrate the chips we measured the loss and permittivity of reasonably pure DGEBA epoxy resin (DER 332 from Dow Chemicals) over a range of temperatures and frequencies. Data was compared with measurements made on a parallel plate cell using a Electro-Scientific Inst. 707B capacitance bridge. Data showed that from 100 Hz to 1 kHz there was good agreement between the two sets of data.

Our measurements of the cure of epoxy resins were made by mounting the sensor on a TO-8 header into a Teflon® socket and then placing the assembly in an oven. The socket is connected to the sensor interface box by means of an eight-conductor Teflon® cable. A drop of the curing mixture was placed on the sensor and the oven temperature was either ramped or controlled at a set temperature by means of a controller. Sample temperature was taken to be close to the oven temperature for the heat-up rates used in this study. This was verified by placing a thermocouple into the header and comparing the header temperature with the oven air temperature. Deviations were generally less than 1°C.

2.2 Conventional Dielectrometry

Conventional dielectric measurements were performed using an Audrey 380 and test cell and press supplied by Tetrahedron Associates.⁽¹⁰⁾ The dielectrometer which has a frequency range from 0.1 to 100 kHz monitors dissipation factor values from 0 to infinity and capacitance values from 1 to 1,000 pF. Both responses are plotted as a function of time on a

3-channel strip chart; the sample temperature is also plotted. The method used to make the measurements and interpret the results have been described by us.⁽³⁾ The dielectrometer response was calibrated by us using a known series of R-C parallel circuits. Within the $\tan \delta$ range of 0.2 to 10 it was found accurate to within 1%.

3. RESULTS AND DISCUSSION

3.1 Epoxy-Anhydride System

Isothermal reaction rate studies were carried out using a cycloaliphatic epoxy-anhydride resin which has been studied before, using conventional dielectric analysis.⁽⁵⁾ The formulation in pbw is: ERL4221 - 100, hexahydrophthalic anhydride - 100, ethylene glycol - 3, and benzyl-dimethylamine - 1. Figure 2 shows the permittivity (ϵ') and loss factor (ϵ'') for isothermal cure at 160°C and Fig. 3 the resulting values of $\tan \delta$.

Figure 2 shows the initial drop in ϵ'' due to an exponential decay in ac conductivity. Early in the cure ϵ'' is proportional to a constant divided by frequency which indicates that changes can be primarily ascribed to decays in conductivity with little or no contribution from dipolar motion.⁽⁹⁾ The ϵ' graph shows that early in cure ϵ' is much greater than one might reasonably expect. This is because of "blocking" of the electrodes by a pile up of ions at the electrodes during the high conductivity phase of the ungelled resin.⁽⁹⁾ After 30 mins of cure the dipolar dispersion from resin vitrification can be seen in ϵ' and ϵ'' . The $\tan \delta$ data of Fig. 3 shows peaks early in the cure that have been noted with "blocked" electrodes.^(3,5) Such blocking even occurs in parallel plate measurements early in the cure cycle when conductivity is high. $\tan \delta$ data, using parallel plate geometry with a blocked electrode, is given in Reference 5 for this resin system. Frequency dependent peaks in $\tan \delta$ were observed during cure and the time to peak at a given frequency was taken as an inverse measure of the reaction rate. From such data an Arrhenius plot of the relative reaction rate can be plotted, with the slope

of the plot being the activation energy for the reaction. Such a plot is shown in Fig. 4 for parallel plate measurements with an Audrey 380 and from microdielectrometry. Three parallel lines are obtained each indicating the same activation energy (12 kcal/mol) for the reaction. The presence of electrode blocking film, which was a 1 mil polyimide film, resulted in shifting the occurrence of the frequency dependent peaks to longer times; with microdielectrometry the peaks were shifted to even longer times indicating a stronger relative blocking effect. However, this does not reduce the ability of either technique to measure relative reaction rates which can be very useful.⁽³⁾

A problem with the present instrumentation for microdielectrometry is observed in Figs. 2 and 3. As the loss factor values fall below about .2, during later stages of cure, there is observed a large amount of scatter in the data. This is due to inherent limitations in the gain-phase meter, where noise becomes significant at low loss levels.

3.2 Epoxy-Aromatic Amine Systems

A multifunctional epoxy resin MY720 from Ciba-Geigy was cured with an aromatic amine-diaminodiphenyl sulfone (DDS) - using 50 pbw of the amine for 100 parts of the resin. MY720/DDS systems are commonly used with other additives in graphite and aramid composites. The resin mixture was subjected to a cure cycle that might be typically used to cure such composites in an autoclave. Figure 5 shows $\tan \delta$ data obtained for several frequencies while monitoring the cure using a microdielectrometer and Fig. 6 shows a $\tan \delta$ data using an Audrey 380 with parallel plate measurements and a blocked electrode.

The two figures show very similar results as far as the various transitions are concerned. Differences in magnitude of the response (particularly at large $\tan \delta$ values) should be ignored because of differing blocking mechanisms in the two systems. In Fig. 5 it can be seen that the 1 kHz frequency provides a continuous trace for $\tan \delta$. The lower frequencies however are off scale during the staging period when the conductivity of the resin is very high. This is probably due to the blocking mechanism

discussed earlier (for the anhydride system) because Figs. 7 and 8 show that when ϵ'' is very high (off scale), ϵ' is also very high and off scale.

Figure 5 shows a series of frequency dependent peaks during resin heat up. This transition is caused by the increase in conductivity of the resin as it is heated up. As the resin gels and cures, the loss of conductivity results in another set of frequency dependent peaks in $\tan \delta$. The Audrey 380 data of Fig. 6 shows similar transitions. Such peaks in the $\tan \delta$ response of resin during cure can be used to control the cure and pressure application points during autoclave cure of composites.⁽⁴⁾ One final item of note in Fig. 5 is the much larger $\tan \delta$ value at 1 Hz compared to say 100 Hz; any changes taking place can be observed more readily at the lower frequency. Therefore, it is possible at the lower frequencies to monitor further into cure, well past the gel point.

4. CONCLUSIONS

Microdielectrometry provides a technique for making quantitative measurements of the dielectric properties of a resin during its cure. By monitoring ϵ'' one can determine if the observed responses are due to changes in conductivity or dipole orientation. It extends dielectric analysis to lower frequencies than have been hitherto possible. By making the cure sensor small and surface emplaceable, microdielectrometry removes the problem of parallel plate electrodes intruding into the curing part. Some problems, however, do remain. These have mostly to do with the present packaging of the sensor and future packaging concepts, if realized, should eliminate many problems. The gain phase meter used in the instrumentation produces considerable scatter in the data at very low loss factor levels and an alternative measurement technique would improve the system performance.

5. ACKNOWLEDGMENT

The assistance of MIT in providing the sensor chips is gratefully acknowledged. The advice of Prof. S. Senturia of MIT and the assistance of N. F. Sheppard, Jr. of MIT in patiently improving on the software are both gratefully acknowledged.

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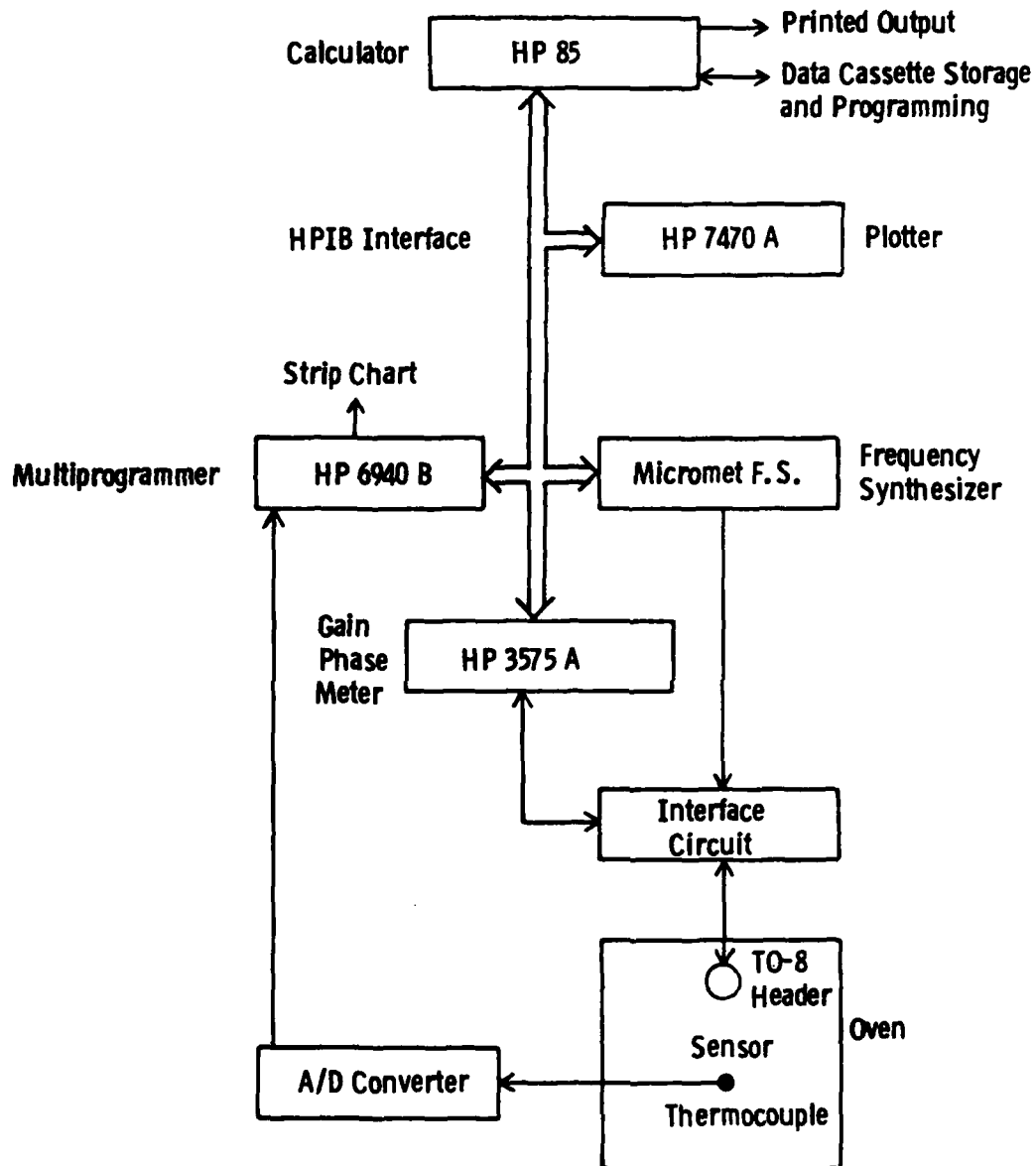


Fig. 1 — Block diagram of measuring system for microdielectrometry

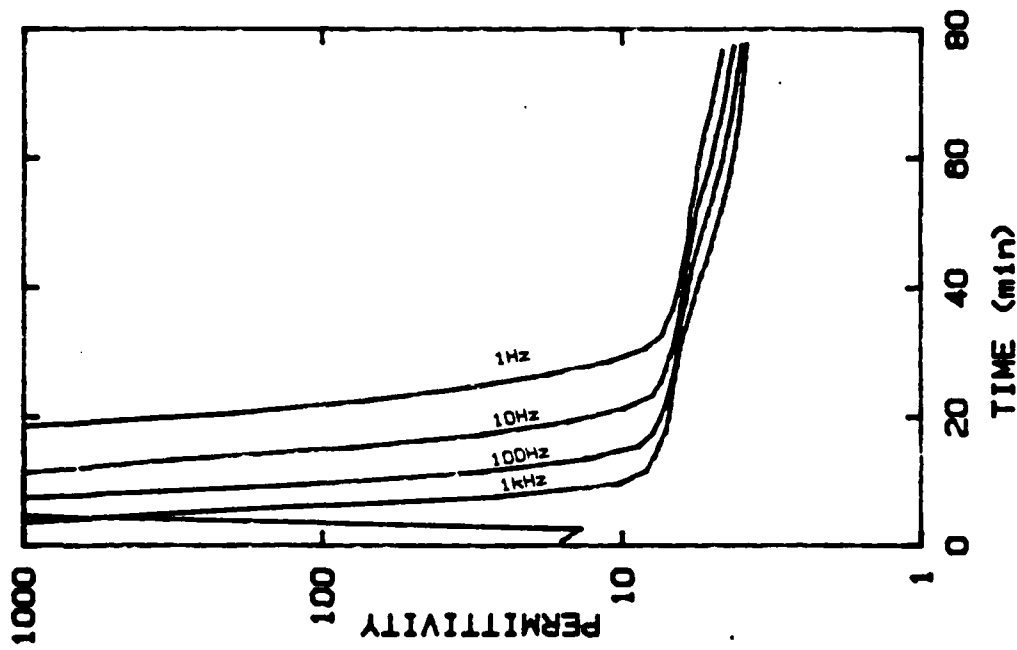
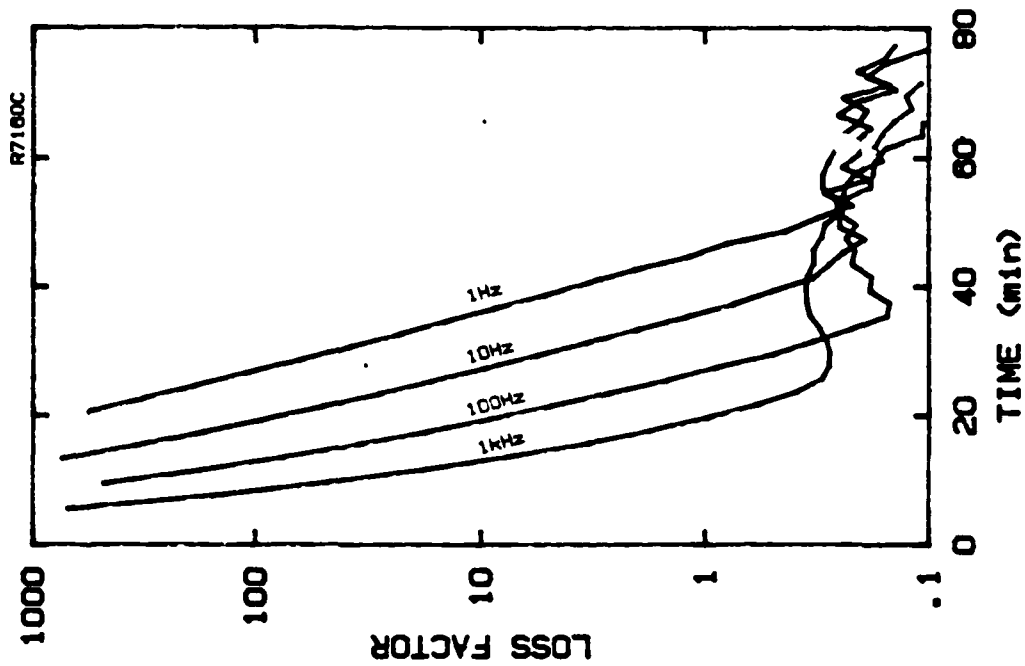


FIG. 2-CURE OF EPOXY/ANHYDRIDE

RESIN SYSTEM AT 160C

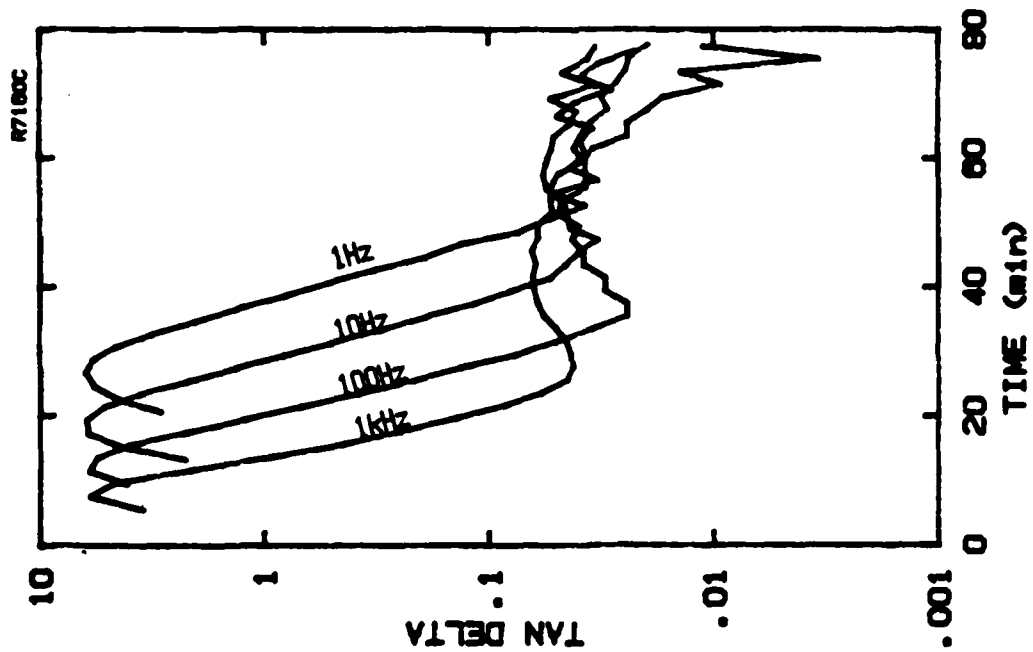


FIG. 3-CURE OF EPOXY/ANHYDRIDE
RESIN SYSTEM AT 180°C

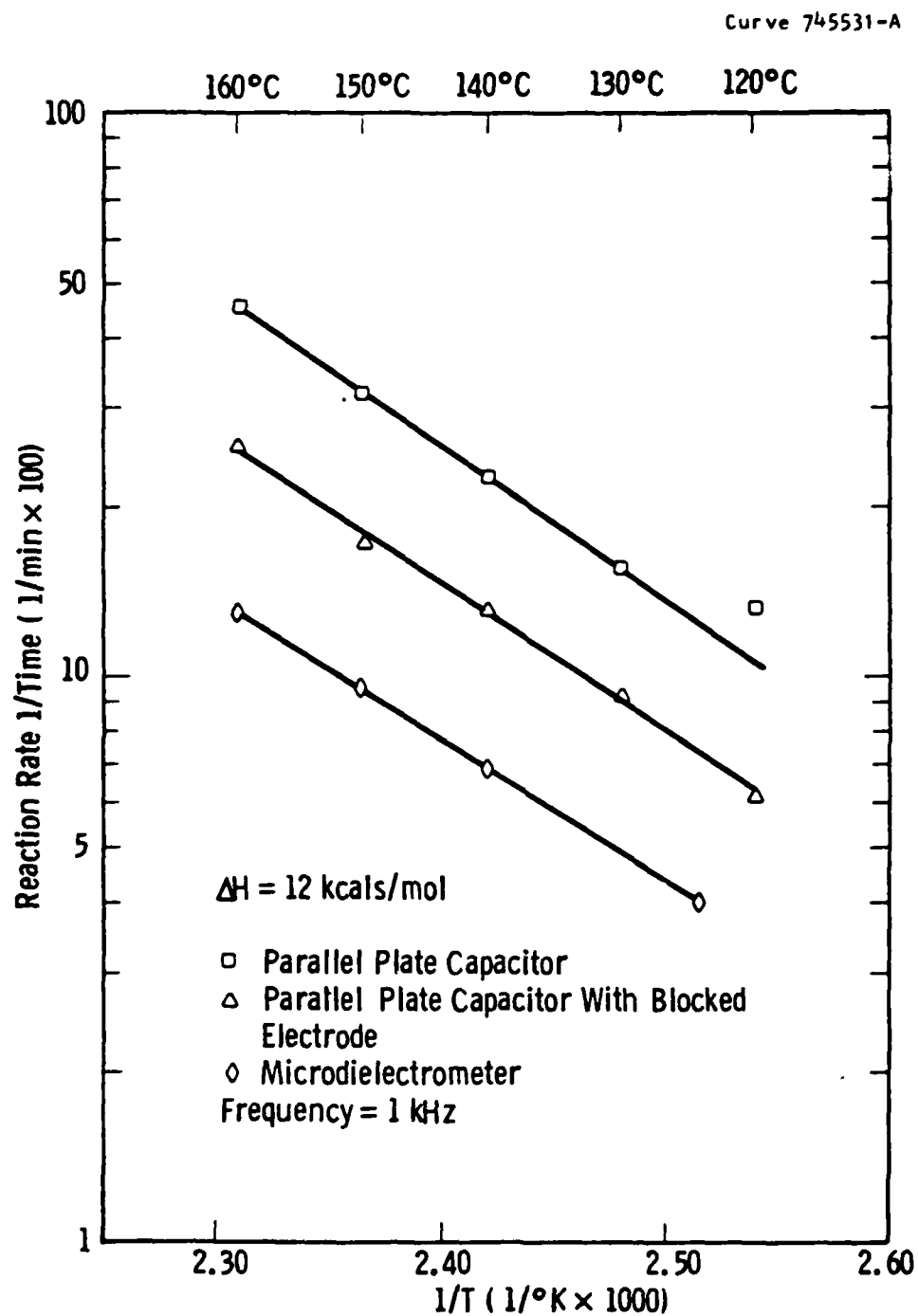


Fig. 4 — Relative reaction rates for the epoxy anhydride system

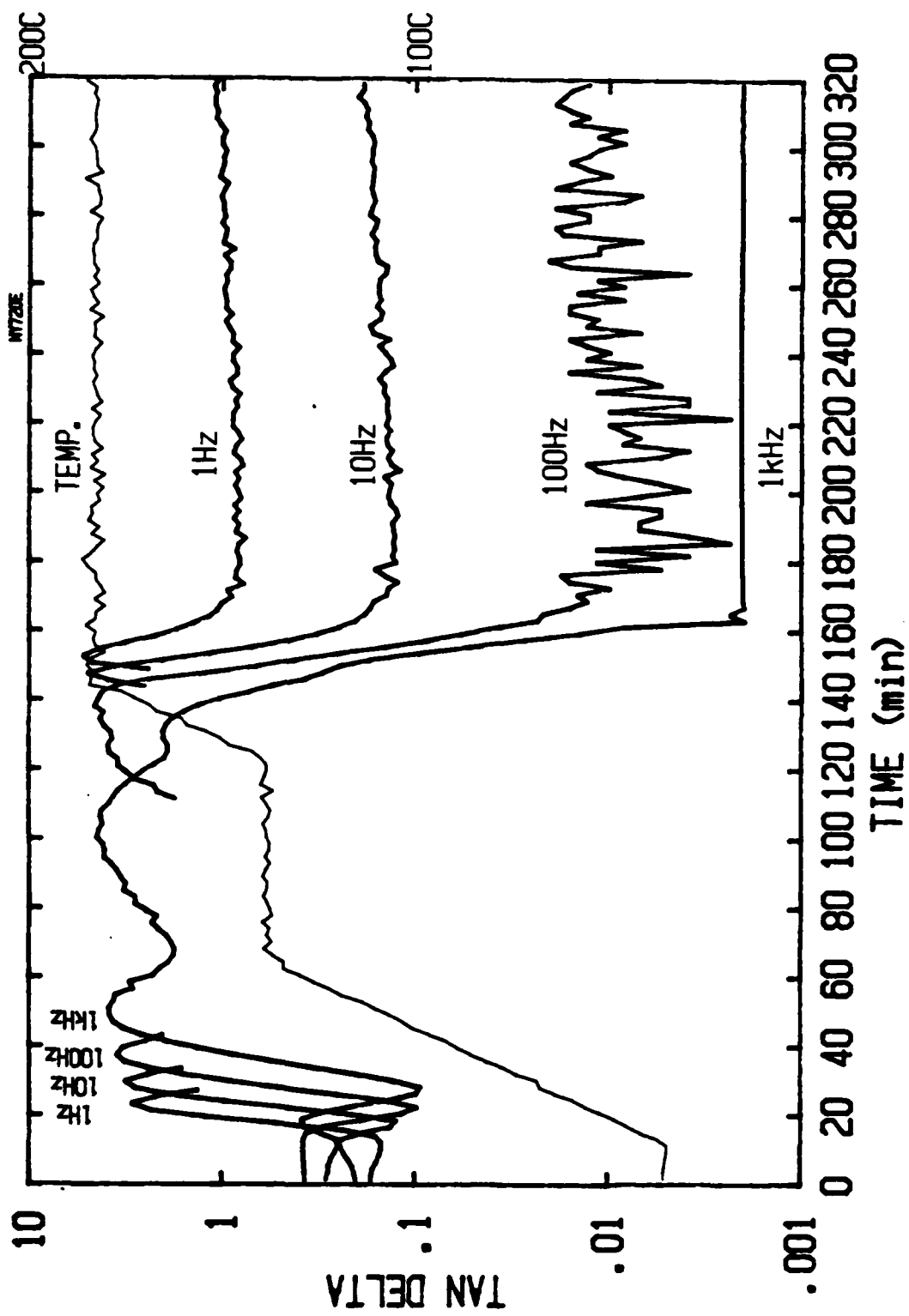


FIG. 5-CURE OF MY720/DDS RESIN SYSTEM

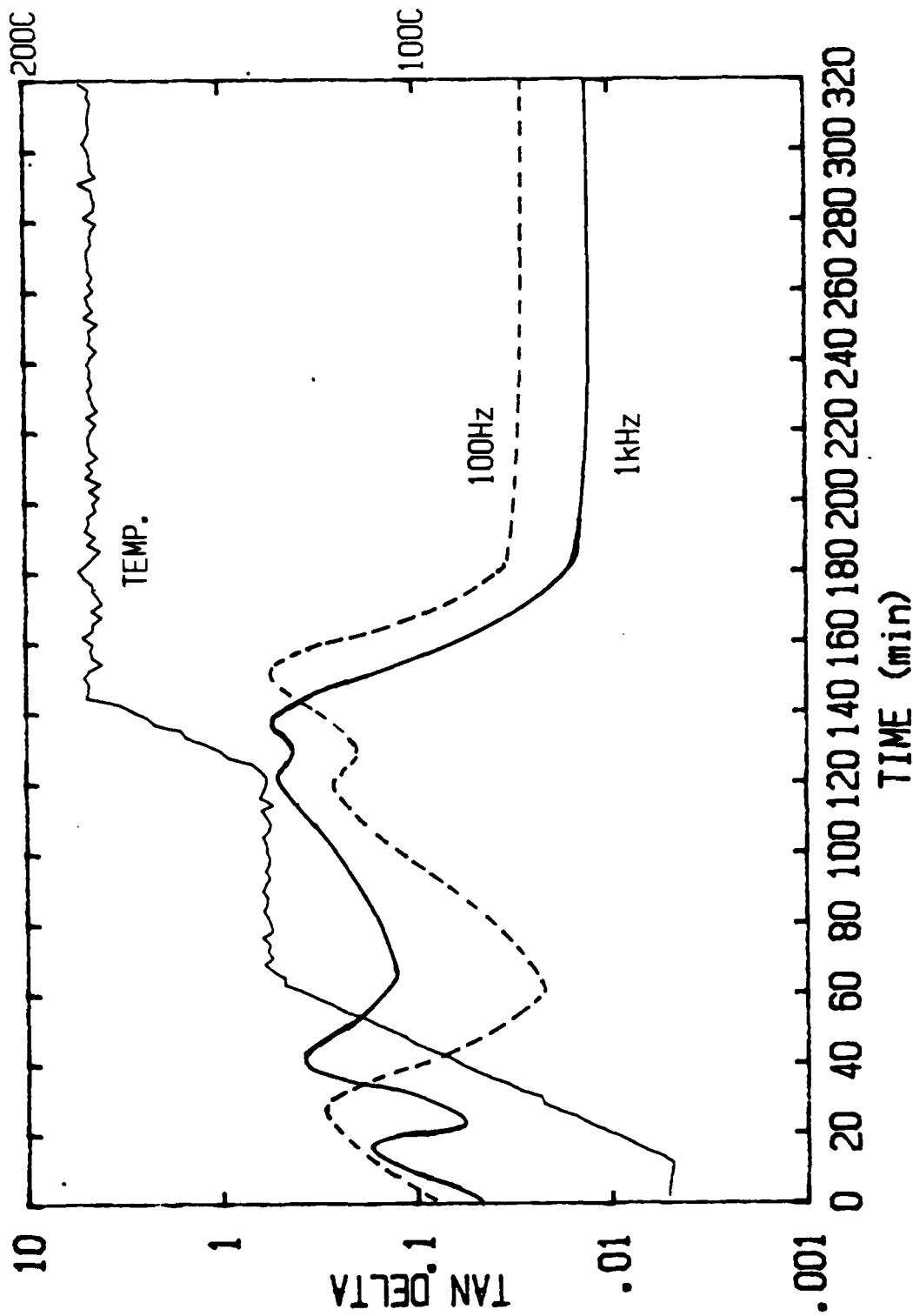


FIG. 6-AUDREY 380 DATA FOR CURE OF
MY720/DDS RESIN SYSTEM

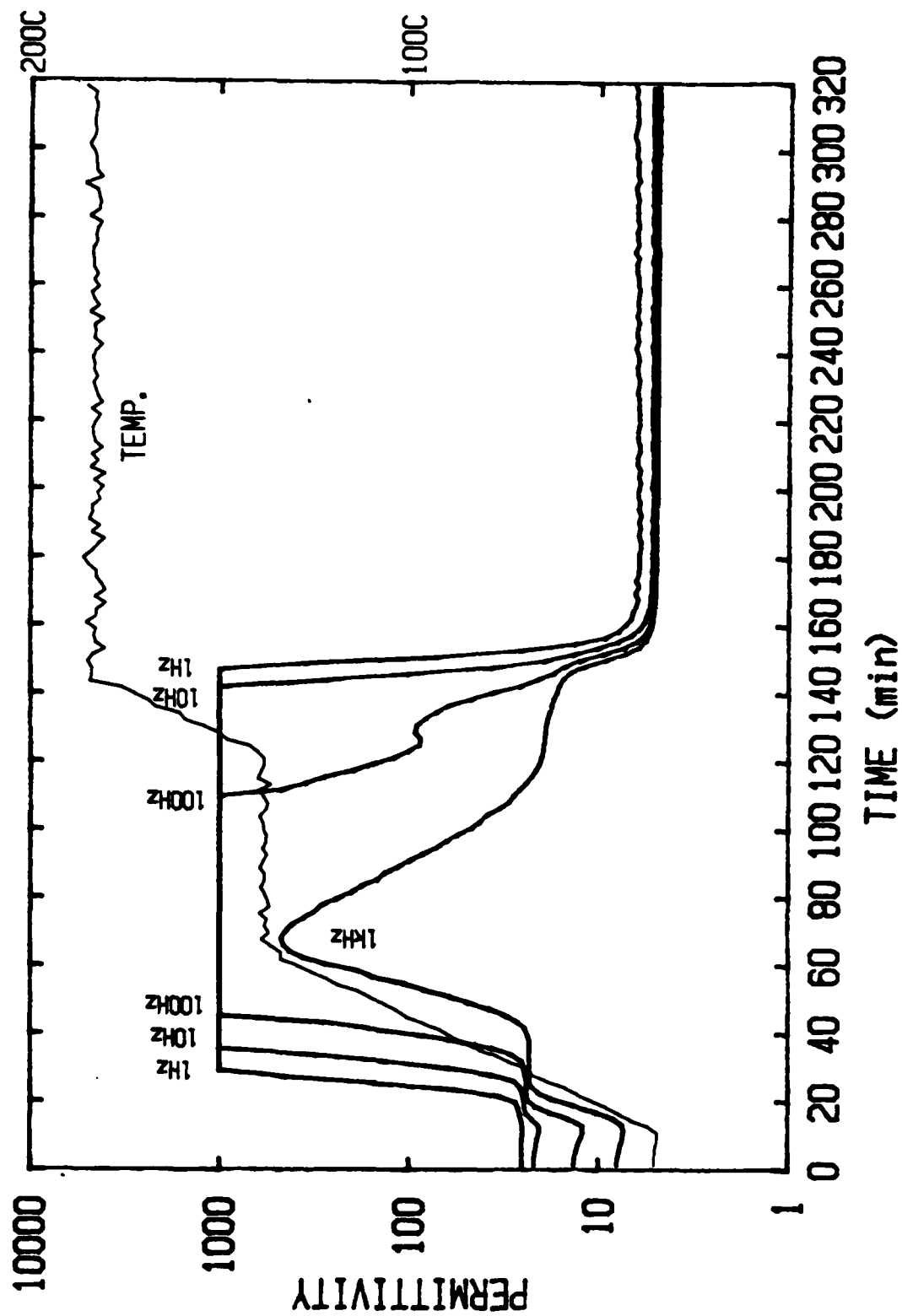


FIG. 7-CURE OF MY720/DDS RESIN SYSTEM

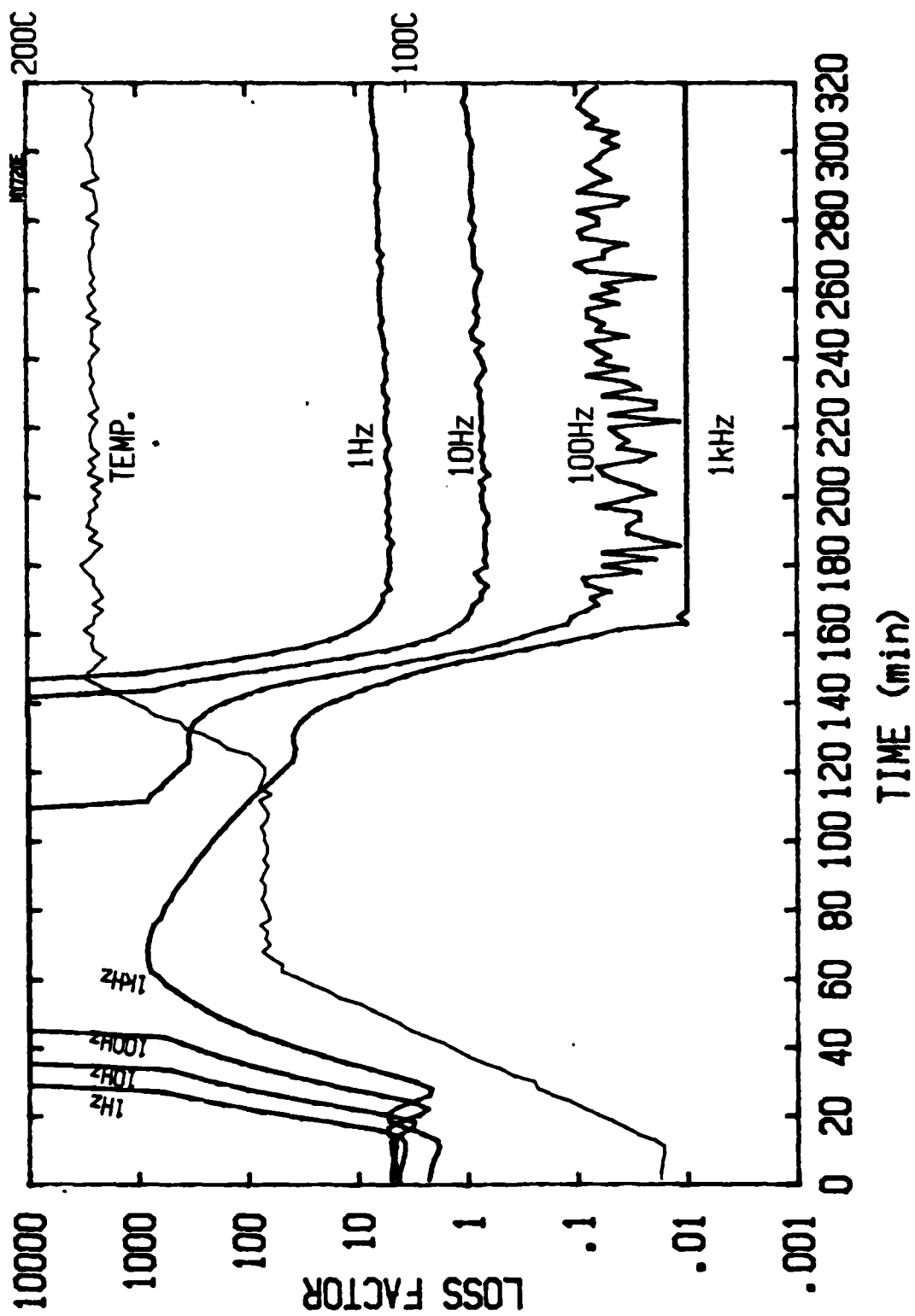


FIG. 8-CURE OF MY720/DDS RESIN SYSTEM

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